Temperature dependence of absorption in ice at 532 nm

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A YAG laser was used to emit nanosecond pulses of light at 532 nm at depths from 1185 to 2200 m in Antarctic ice, corresponding to temperatures increasing from 229 to 249 K. From the timing distributions of photons arriving at phototubes at distances up to 100 m and at similar depths, the scattering and absorption coefficients were measured, and the temperature dependence of absorptivity at 532 nm was determined. Despite the absorptivity being many orders of magnitude lower at 532 nm than in the near ultraviolet and near infrared, the fractional increase of absorptivity, $a^{-1}\mathrm{d}a/\mathrm{d}T = 0.01\ \mathrm{K}^{-1}$, was the same in the visible, ultraviolet, and infrared. Analysis of published data at other wavelengths shows that $a^{-1}\mathrm{d}a/\mathrm{d}T$ is $\sim 0.01\ \mathrm{K}^{-1}$ from 175 nm to ~1 cm, above which it increases strongly from 1 cm to 10 m. That temperature dependence applies only in regions not close to absorption bands.

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1. Introduction

The temperature dependence of absorption of electromagnetic radiation is of great practical importance. Absorption in the ultraviolet has been used to probe the electronic band structure.[1] The slope of the steep Urbach tail in the ultraviolet decreases with increasing temperature. The location and shape of infrared absorption bands that are due to intramolecular stretching, bending, libration, and their overtones depend on temperature. Water ice, the most important component in astrophysical ices, is observed in many interstellar, circumplanetary, and cometary spectra, on the surfaces of Mars and Europa, and in terrestrial clouds. Provided that high-quality laboratory data exist, ice spectra can be a useful probe of the temperatures encountered by dust grains and their icy mantles.[2–4] In the far infrared the strength, sharpness, and peak frequency of intermolecular translational and rotational bands for ice show a temperature dependence, and laboratory data have been used to determine the mean thickness of ice in Saturn's rings from the measured thermal component of the brightness temperature of the rings.[5] At radio frequencies airborne and surface radar analyses are used to locate subglacial lakes, to map bedrock and sediments, and to trace isochrons that are due to volcanic and other highly conducting impurities in ice at various depths. The temperature dependence of absorptivity must be taken into account in the interpretation of such data. The AMANDA (Antarctic Muon and Neutrino Detector Array) collaboration[6] has deployed photomultiplier tubes in deep ice at the South Pole to study interactions of high-energy neutrinos. To measure trajectories of the products of these interactions (muons and electromagnetic cascades) by means of their Cherenkov radiation, one needs to take into account scattering, absorption, and the temperature dependence of absorption at wavelengths in the visible and near ultraviolet. The RICE (Radio Ice Cherenkov Experiment) collaboration[7] is developing a method for detecting ultrahigh-energy neutrino interactions in ice by detecting coherent radio Cherenkov radiation from electromagnetic cascades. The thickness of ice over which radio emission can be detected, and thus the scale of such an observatory, depends on the temperature dependence of absorptivity.

2. Absorption of Light at 532 nm as a Function of Depth in Ice at the South Pole

We now present, for the first time, data on the temperature dependence of absorption by ice in the visible. Figures 1(a) and 1(b) show measurements of effective scattering coefficient and absorption coefficient (absorptivity) at 532 nm, made as a function of depth in deep glacial ice near the South Pole Station, taken from Ref. 8. A 532-nm YAG laser at the sur-

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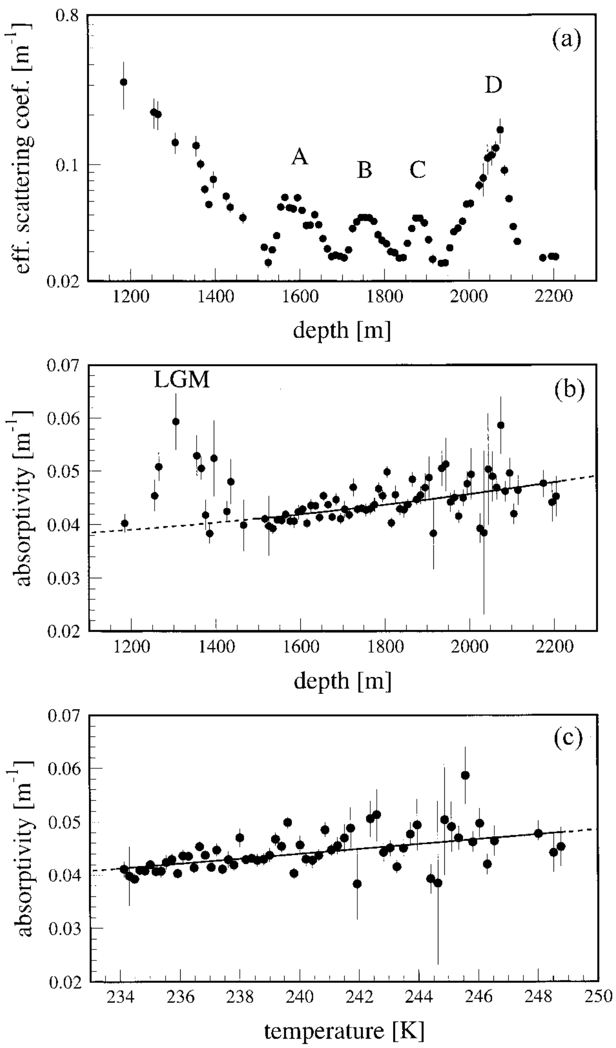

Fig. 1. (a) Effective scattering coefficient of light at 532 nm as a function of depth in ice at the South Pole. (b) Absorptivity of light at 532 nm in the same depth interval. (c) Absorptivity as a function of temperature by use of AMANDA data on temperature versus depth. Straight-line fit is given in Eq. (2).

face was used to send nanosecond light pulses through optical fibers down to diffusing balls embedded in the ice at depth intervals of 10–20 m. The arrival times of light pulses were recorded by photomultiplier tubes embedded in the ice at depths from 1185 to 2200 m and at horizontal distances up to ~100 m from the sources. From the photon arrival time distributions, both scattering and absorption coefficients were extracted as described elsewhere.[8] The long path lengths in ice made it possible to determine the small values of absorptivity with high precision and accuracy. The ice is polycrystalline, is extremely pure, and has a density of ~0.916 g cm^{-3}. Our colleagues and we have previously shown that the contributions of pure ice and of embedded dust grains to absorption of visible light are additive,[9,10] in accord with Mie theory, and their relative contributions change from what is dominantly due to dust at wavelengths between ~200 and ~500 nm, to what is dominantly due to pure ice at wavelengths longer than ~500 nm and at wavelengths shorter than ~200 nm. At wavelengths of 337 and 470 nm where absorptivity is dominated by dust, we studied absorption as a function of depth and found peaks and valleys at various depths. The peaks were due to layers of high dust concentration that track the well-known dependence of atmospheric dust concentration on the Earth's climate.[11]

In this study we analyze data at 532 nm, where intrinsic absorption by ice dominates over absorption by dust except at high dust concentrations that occur during cold climatic conditions. This insensitivity to dust at 532 nm made our discovery of a temperature dependence of intrinsic absorption possible.

In Figs. 1(a) and 1(b), the peaks labeled LGM, A, B, C, and D are due to increases in light scattering and absorption by horizontal bands of excess dust concentration. In Fig. 1(a), the LGM peak is masked by the contribution of air bubbles that scatter light without absorbing it. Scattering by bubbles decreases rapidly with depth in the glacial ice caused by compression of the bubbles and their gradual conversion into a solid clathrate phase. At depths from the surface down to ~1400 m the dominance of the bubbles rules out studies of scattering by the dust. At depths below 1400 m all bubbles convert into clathrate crystals, which are practically invisible because their refractive index is almost exactly the same as that of normal ice. In Fig. 1(b) the absorptivity shows an excess between 1200 and 1450 m, with a peak at 1300 m. From ~1450 to 2200 m the absorptivity is featureless but increases approximately linearly with depth (see below for a more quantitative rate of increase).

In a recent paper[12] we identified the peak in Fig. 1(b) labeled LGM, at depth 1300 m, and also subpeaks labeled A, B, C, and D with corresponding peaks in dust concentration measured in deep ice cores from two Antarctic sites: Vostok Station and Dome Fuji. Using the age versus depth relationships established for Vostok and Fuji and matching our peaks with theirs, we derived the age–depth relation for South Pole ice.[12] The dust peak at the LGM corresponded to the last glacial maximum, 22,000 years before now, and was higher than at any other time in the last 420,000 years, with a value ~50 times greater than in the last ~15,000 years.[11] It remained extremely high for a time interval consistent with our observation of an excess in absorption from ~1200 to 1450 m. The next highest dust peak [corresponding to D in our Fig. 1(a)] was recorded in both ice cores at depths corresponding to a time ~65,000 years ago. For Vostok the ratio of that peak to the peak at the LGM was ~0.5; for Fuji the ratio was ~0.3; for Greenland ice cores the dust peak corresponding to 65,000 years ago was ~0.4. At the South Pole we conclude that the scatter of points in Fig. 1(b) could well hide a ratio of dust at D to dust at LGM comparable with that at Fuji.

To study the weak temperature dependence, we focus attention on the absorption data at depths from

1450 to 2200 m. In Fig. 1(c) we display the data at these depths as a function of ice temperature. Temperature as a function of depth in ice at the South Pole was measured by the AMANDA collaboration with embedded thermistors. At depths between 800 and 2375 m, ice temperature fits a quadratic dependence:

$$T(\mathrm{K}) = 221.5 - 0.00045319z + 5.822 \times 10^{-6}\, z^2. \tag{1}$$

We assume the temperature dependence of absorptivity at depths from 1500 to 2200 m to be linear, which leads to a weighted least-squares fit:

$$a(z) = (-0.066 \pm 0.013) + (0.458 \pm 0.056) \times 10^{-3} T\ (\mathrm{K}). \tag{2}$$

This is more than 8σ from a slope of zero. The curve through the data in Fig. 1(b) was obtained by use of Eqs. (2) and (1). Taking the average value of absorptivity to be 0.045 m^{-1}, the value at the depth halfway between 1500 and 2200 m, we find a fractional change in absorption per kelvin at 532 nm:

$$\langle a \rangle^{-1} \mathrm{d}a/\mathrm{d}T = 0.010 \pm 0.0012\ (\mathrm{K}^{-1}). \tag{3}$$

From known values of volume expansion and isothermal compressibility for ice,[13] we calculate that at constant pressure the increase in temperature from 234 K at 1500 m to 249 K at 2200 m would lead to a fractional expansion of 0.0022, whereas the increase in pressure would lead to a fractional contraction of 0.0014. Beyond any effect of a change in intermolecular spacing on absorption, thermal activation or kT plays the dominant role. For example, the effect of the temperature increase ($\Delta T \approx 15$ K) with depth on the static dielectric constant, ϵ_s, would be $\sim 10^2$ times greater than the effect of the pressure increase ($\Delta p = 53$ bars)[14]; the effect of the temperature increase on the Debye relaxation time, τ_D, would be ~300 times greater than the pressure effect[14]; the shift of resonant frequency of translational lattice vibrations, v_T, at 218 cm^{-1} as a result of temperature increase would be six times greater than that due to the pressure increase[15]; and the shift of resonant frequency of O—H stretching vibrations, v_1, at 3130 cm^{-1} as a result of temperature increase would be 14 times greater than that due to the pressure increase.[16] In comparing the temperature dependence of absorption of visible light with absorption at other wavelengths measured at constant pressure, we ignore the minor role of the increase of pressure with depth.

3. Temperature-Dependent Absorptivity Across the Electromagnetic Spectrum

Figure 2 shows measured values of the fractional increase in absorptivity with temperature as a function of wavelength for wavelengths from ~175 nm up to 8.6 m. Table 1 gives the sources of the data, along with comments. Impurity content of samples affects temperature dependence: samples with saline impurities tend to have a higher absorptivity and a greater temperature dependence than do specially purified samples. Samples with a high content of bubbles, cracks, and other defects give poorly reproducible results. We have given preference to data for samples of high purity, to data obtained with modern instruments, and to data that have superseded older data for reasons that have been provided in the references. Only for radio wavelengths,

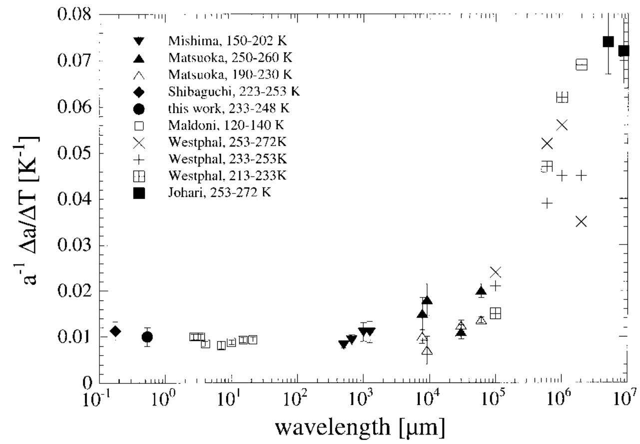

Fig. 2. Fractional increase in absorptivity with temperature of ice as a function of wavelength for electromagnetic radiation not close to absorption bands.

Table 1. Sources of Data and Comments

Wavelength	T_h (K)	T_l (K)	Ref.	Comments on References
173–178 nm	253	223	1	Individual data points not shown; only fitted curves
532 nm	248	232	8	Pressure covaries with temperature
2.7–21 μm	140	120	2	Errors estimated by comparing directly deposited samples with samples cooled from a higher temperature
0.05–0.125 cm	202	150	5	Propagation of errors provided in Ref. 5; supersedes Ref. 17
0.77–6 cm	260	250	18	Propagation of errors provided in Ref. 18; supersedes Ref. 19
0.77–6 cm	230	190	18	Propagation of errors provided in Ref. 18; supersedes Ref. 19
0.1–2 m	233	213	20	No errors given; spread with T is a measure of error
0.1–2 m	253	233	20	No errors given; spread with T is a measure of error
0.1–2 m	272	253	20	No errors given; spread with T is a measure of error
5–8.6 m	272	248	21	Errors inferred from spread of points

where the temperature dependence is largest, do the data depend strongly on the temperature interval chosen. Throughout the near and far infrared, absorption bands show a complicated dependence on temperature.[2–4,22,23] With higher temperature, the shapes of absorption bands become less sharp, the strengths of some bands decrease, the absorption in continuum wavelengths increases, and the centers of some bands shift to shorter wavelengths. For the data in Fig. 2, we avoided regions close to absorption bands.

4. Discussion

The weak dependence of absorptivity on temperature, $a^{-1}\mathrm{d}a/\mathrm{d}T$, is in stark contrast to the extremely strong dependence on wavelength. For example, in the visible the AMANDA collaboration showed[24] that absorptivity decreases nearly 10 orders of magnitude from a plateau in the near ultraviolet to a minimum in the visible at around 400 nm and then increases by 9 orders of magnitude in the infrared, whereas, as Fig. 2 shows, there appears to be no change in $a^{-1}\mathrm{d}a/\mathrm{d}T$ through this region. This is the most intriguing result of this study.

It is only through a special set of circumstances that our observation of a temperature-dependent absorptivity of ice in the visible was feasible. Early measurements of absorptivity in the visible on laboratory samples of ice[25] gave values of as much as an order of magnitude higher than we found in deep South Pole ice, because of their failure to separate scattering losses from true absorption and because of impurity contributions. Antarctic ice has the advantages of high purity, long annealing time, and unlimited volume, and our method based on the timing distribution of nanosecond pulses from a YAG laser allows scattering and absorption to be determined separately.

To our knowledge this is the first time that temperature dependence of absorptivity of ice at continuum wavelengths has been presented on a single graph for electromagnetic radiation spanning eight decades of wavelength. Despite differences in the theoretical basis for the role of temperature in absorption at different wavelengths, the magnitude of the effect is nearly constant at $\sim$1%/K up to $\sim$1 cm, then increasing strongly from 1 cm to 10 m. The value for visible light is, within errors, the same as for ultraviolet and infrared. We should reemphasize that the temperature dependence of 1%/K does not apply in the vicinity of an absorption band but only in the continuum.

Unfortunately, the theory of the interaction of electromagnetic radiation with molecular crystals is not on firm enough ground to make quantitative predictions of temperature dependence of absorptivity. The best that has been done is to apply general principles, for example, Debye's treatments of lattice vibrations and of relaxation processes, but with temperature-dependent parameters that have to be fitted to experimental data.

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